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CHEMISTRY OF SYNTHETICS IN THE USSR -- HIGH POLYMER RESEARCH AND SYNTHETICS TECHNOLOGY

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[Following is the translation of an article by Raimund Ulbrich in Osteuropa-Naturwissenschaft (Eastern Europe - Natural Sciences), No 1-2, Stuttgart, 1958, pages 31-39.]

At the session of the Central Committee CPSU, on 6 and 7 May 1958, N. S. Khrushchev undertook to present a report "Accelerated development of chemical industry, especially regarding the manufacture of synthetics and the utilization of these materials to satisfy the needs of the population and the needs of the national economy". On the basis of this deliberation the plenum prepared a resolution containing the following statements, among others (Pravda, 9 May 1958):

"The accelerated development of the chemical industry is of great importance in solving this task. The Soviet Union now holds second place in the world in volume of output of chemical products. However, the present level of production and the rate of development of the chemical industry, especially in the output of synthetic materials, still do not satisfy the increased demands of the national economy.

The use of synthetic materials will make it possible to increase considerably the production of clothing, footwear, fabrics, and household and other goods. Products made from these materials are not only not inferior but are often considerably superior to products made of natural raw materials.

The measures for the accelerated development of the chemical industry and particularly the production of synthetic materials that have been worked out by the Presidium of the Central Committee CPSU, and the USSR Council of Ministers and set forth in the report by Comrade N. S. Khrushchev provide for increasing capacities for producing artificial and synthetic fibers to 4.6 times, plastic and synthetic resins to eight times and synthetic rubber to 3.4 times the 1957 level by the end of 1965.

The achievement of mass production of synthetic materials in a short time will assure an increase in the production of fabrics from

artificial and synthetic fibers in 1965 as follows, in comparison with 1957: wool fabrics -- 2.3 times, silk -- 1.75 times, cotton -- six times, knitwear made of artificial and synthetic fibers -- more than nine times, hosiery -- 3.2 times, artificial karakul -- 14 times, footwear of artificial leather -- 2.3 times, and the production of crepe-sole footwear -- 40 times.

By developing the production of synthetic materials, the output of woolen fabrics will be increased to 500 million meters in 1965, including 450 million meters of fabric from artificial and synthetic fibers; the output of silk fabrics to 1,485 million meters, including 1,237 million meters of fabric from artificial and synthetic fibers, the output of cotton fabrics to 480 million meters, using artificial and synthetic fibers; knitwear production to 940 million items, including 588 million items with artificial and synthetic fibers; the output of artificial karakul to five million square meters; and the output of footwear will be increased to 515 million pairs, including 93 million pairs of artificial leather and 233 million pairs with crepe-soles."

These highly set planned goals for the chemical industry of course place great demands on the basic research and technology of synthetics. The basic research includes especially the physical chemistry of high polymers. In the last years the Soviet Union has worked very intensively in this area.

The number of the published reports is very considerable in the many scientific and technical periodicals and the number increases every month. Although no statistics have been gathered pertaining to these publications, a careful estimate should show that the number of scientific and technological reports published in the USSR pertaining to high polymers and synthetics is about a half to two-thirds of the total number of the same published in the rest of the world. In the USSR, however, there is no special publication for synthetics comparable to the German publication Kuntstoffen or to the American Modern Plastics or, finally, to the British Plastics. Nor is there in the USSR a publication exclusively for high polymer basic research, such as, for example, the Journal of Polymer Science or the Makromolekulare Chemie. The respective reports are scattered in the many special publications for chemistry and physics. The more important reports appear especially in the following periodicals: Dokladi Akademii Nauk SSSR (Reports of the Academy of Sciences, USSR), Izvestiya Akademii Nauk SSSR (News of the Academy of Sciences, USSR), Kolloidniy Zhurnal (Colloid Journal), Khimicheskaya Promishlennost' (Chemical Industry), Khimicheskaya Nauk i Promishlennost' (Chemical Science and Industry; a publication of the Mendeleyev Society).

Research Institutes

The basic research on high polymers is concentrated mainly at two institutes of the Academy of Sciences of the USSR: at the Institute for Macromolecular Compounds, Leningrad, and at the Institute for

Macromolecular Compounds, Leningrad, and at the Institute for Elemental-Organic Compounds, Moscow, the latter being concerned also with more extensive problems.

The Institute for Macromolecular Compounds, at present [1958] directed by Prof S. M. Danilov, corresponding member of the Academy of Sciences, has nine laboratories as follows:

1. The chemical laboratory for cellulose research directed by the director of the Institute, Prof Danilov.

2. The chemical laboratory directed by Prof V. A. Dolgoplosk. It works on the basic processes of polymerization (i.e., the reactions which combine single molecules into long chains) with the elementary mechanisms of the chain degradation as well as with the cross-linking as influenced by reversible red-ox [i.e., reducing -- oxidizing] systems.

3. The laboratory under the direction of Prof M. M. Koton investigates especially the polymerization of vinyl compounds and the properties of epoxy resins.

4. In the laboratory of Prof A. A. Vansheidt the correlation between the molecular structure and the macrophysical properties of polycondensates (e.g., polyamides) is being examined.

5. One of the problems examined by the physical chemistry laboratory directed by Prof S. E. Bresler pertains to the kinetics of polymerization and to the basic processes of degradation and cross-linking of high polymers; the other problem investigated in this laboratory is the mechanism of ion exchange.

6. The second physical chemistry laboratory is directed by Prof V. N. Tsvetkov and it is equipped for research on dilute solutions of high polymers; as is common also elsewhere, the physical methods used here are based on light scattering, diffusion, and streaming birefringence. The investigation of dilute solutions of high polymers has basic theoretical significance. Therefore the investigations under Prof Tsvetkov have a strongly theoretical slant; his coworkers, without exception, have specialized mathematical education.

7. The laboratory for research on the structure of high polymers is directed by the noted Soviet physicist Prof M. N. Volkenshtein; it has a special division for ultraspectroscopy under the direction of Dr V. N. Nikitin. The following problems are investigated: relaxation phenomena, theoretical interpretation of the so-called second order transformations, special problems concerning cis-trans isomerism of polymers, hydrogen bonding in polyamides and cellulose, crystallization of polyethylene, the mechanism of solution in polar solvents, and others. The predominating part of the theoretical investigations in this laboratory is the work by Prof Volkenshtein personally, most of the experimental investigations being inspired by him; his laboratory employs mainly physicists and mathematicians; the laboratory should be very richly supplied with instruments.

8. A laboratory for electrical measurements, under the direction of Prof G. P. Mikhailov, and

9. A laboratory for research on the mechanical properties of polymers, under the direction of Prof Kuvshinskiy.

The Institute for the Elemental-Organic Compounds in Moscow is directed by the president of the Academy of Sciences of the USSR, A. N. Nesmeyanov. One of the main divisions of this institute is used for the chemistry and physical chemistry of high polymers; it is directed by Academy Member V. V. Korshak. Numerous publications appear yearly published under V. V. Korshak's name; he is personally in charge of the Section for Polycondensates. The section for carbon chain polymers is under Prof G. S. Kolesnikov and the physical chemistry section under Prof G. L. Slonimskiy. To the well known members of this Moscow institute belong also Professors A. Y. Kitaigorodskiy (X-ray structure), L. V. Obreimov (optics), and M. O. Korshun (analytical laboratory). The chemical character of research is strongly stressed in the Moscow institute. The intensive cooperation encouraged among chemists, physicists and mathematicians that showed considerable success at the beginning in Leningrad, has been only later launched also in Moscow. (Ulbrich, R., Kunststoffe, No. 47/g, p. 545 (1957).

In both institutes the proposed research problems should be realted to the further development of technological methods, as it is the prevailing characteristic orientation of science in the USSR. Basic research is not conducted without reference to practical applications. Sectional distribution of larger theoretical problems to coordinated working groups, with maintenance of objective and unified execution of the scientific research theme and the maintenance of very high requirements regarding the scientific, especially mathematical-theoretical preparation of coworkers, are further characteristics of the scientific research methodology in the USSR.

In the framework of the Academy, there are certain high polymer research problems investigated also in the Selinskiy Institute for Organic Chemistry. Next to these there exist the following large research institutes:

The Scientific Research Institute for Polymer Synthetics (Nauchno-Issledovatel'niy Institut Polimerisazionnikh Plastikov -- NIIPP) with branches in Kemerovo, Nizhniy Tagil, Novosibirsk, and Sverdlovsk. The main problem of the Institute is the development of synthetics which show high resistance to low and high temperatures. An additional newer problem is the development of inorganic polymers. (Garbar, M. Y., Khimicheskaya Promishlennost', p. 397, Oct/Nov 1957.)

In the L. Y. Karpov Institute for Physical Chemistry, research on merization processes should be considerably expanded, as well as the work in colloid chemistry and in chemistry of metalo-organic compounds. However, in the future the research on radiation effects on the chemistry of high polymers and general investigation of possibilities for application of radiation in chemistry will be the main problems of this institute.

Further, there are several institutes which are working on raw materials and on monomer initial materials for synthetics; they are believed to be under the direction of Ministry for the Chemical Industry. Here

belongs the Leningrad Scientific Research Institute for Petroleum Utilization (Leningradskiy Nauchno-Issledovatel'niy Institut po Pererabotke Nefti -- Len. N. I. I.), the Research Institute for the Alcohol Industry [sic] (Vsesoyuzniy Institut Gidroliznoy i Sulfitno-Spiritoviy Promishlennosti -- VNIIGS) and the Central Chemical Research Institute of the Forest Administration [sic] (Tsentral'niy Nauchno-Issledovatel'skiy Leso-Khimicheskiy Institut -- TsNILKhI). Lately the production and utilization has been extensively increased of synthetics which contain synthetic glass fibers (ethoxylene resins, unsaturated polyesters). These synthetic fibers must fulfill certain technical requirements; therefore there is in the USSR the Scientific Research Institute for Glass Fibers (Vsesoyuzniy Issledovatel'skiy Institut Steklyannogo Volokna -- VNIISW). Regarding its importance in the development of synthetics the affiliation of this institute with the Ministry for the Chemical Industry is considered necessary. (Ulbrich, R., Kunststoffe, No 47/g, P 545 (1957).

Further, high polymer research is also conducted in the USSR at the university institutes and at the prominent industry institutes. Of course, the respective faculty members have a stronger influence on the type and level of research done at the university institutes than at the above named special institutes which are subjected to certain specific directions. Several professorial chairs have achieved greater importance in high molecular research: the professorial chair for macromolecular compounds at the University of Leningrad -- directed by Prof A. Yakubovich; the professorial chair for artificial and synthetic fibers at the Moscow Textile Institute -- directed by Prof Z. A. Rogovin. Among the best known personalities in high molecular research in the USSR are Professors S. M. Lipatov, Topchiyev, Andrianov, lately deceased Prof Strepikhayev and Prof G. S. Petrov, the old pioneers of the Soviet synthetics industry. Naturally, the technical goals are placed in foreground in the industrial laboratories. The scientific-theoretical aspects appear here only on the side. At present a large research center for high polymers and synthetics is being constructed at the industrial plants in Vladimir. Lively impressions about personalities engaged in high polymer research in Moscow and Leningrad and about their methods are given by H. F. Mark in his recent report regarding his visit to the Soviet centers of high polymer research. (Mark, H. F., Modern Plastics, Vol 35, No 11, p 111 (1958)).

Research Methods

A survey of problems in the area of high polymer research worked on during the last years in the USSR shows that the approach to this subject has the same formulation of questions as in Western Europe and in the USA. In the USSR we do not see any great problem of theoretical importance that would not be considered by the respective specialists in the Western world. The various theoretical and experimental research methods, including the most modern ones presently used in the USSR (as much as can be determined from the specialized literature) correspond

to the general status of knowledge in the Western world. It is so with the mathematical-theoretical methods of statistical thermodynamics, it is also so, just to show two examples, with the modern physical-experimental methods of magnetic nuclear resonance and with the radioactive isotope labeling of chemical compounds; these methods are utilized and developed further in the USSR just as in Western Europe, the US and Japan. In comparing the USSR with Germany specifically, perhaps the more intensive attention to mathematical-theoretical analysis in the high molecular research in the USSR is striking. The great number of Soviet publications signifies that also in the high molecular research field an unbelievably large number of personnel is being employed in the USSR, as compared with European standards. However, a really inspired leadership can be seen only in some. There are only a few names which repeatedly appear in publications. The greater number of the publications are not above the usual level of dissertations or theses. Often they simply deal with the results of routine measurements. However, there are also investigations which show excellent theoretical knowledge and experimental technique, and the accomplishment of which required devoted work by the whole research team.

According to the rules imposed in the USSR, scientific research must not have a purely academic character, but, regardless of its possibly great importance to scientific theory, it must also at the same time have a relationship to practical application. Often it appears, however, that the obligatory relationship to practical utilization which, according to its character, should be subordinate to basic research, is indeed forced at the end of the discussion. Sometimes the unavoidable reference to the eventual usage for practical application is used as an excuse for the inclusion of research results which, because of their scientific quality, do not have a definite necessity and which are unimportant for the report. In the past few years missing among the published research reports in the USSR in the area of high polymer research are those which would bring forth new basic knowledge, or which would give new impulses to technology and to whole new branches of science. In comparison one should consider in the same line the basic works by Staudinger, the development of new types of synthetics in Germany, the US, and British industrial laboratories, and, especially regarding the last years, the great impulse achieved by the discovery of Ziegler catalysts and with them associated research by Natta on stereospecific catalysis.

Despite all restrictions one should be careful not to underestimate the success of Soviet high polymer research and of Soviet synthetics technology. In judging the real situation in this matter solely on the basis of reports in journals, one cannot be sufficiently careful. For similar reasons, knowledge of Soviet scientific literature is yet very unsatisfactory in Western Europe. In the last months something in this field has been done by the Americans, who issue regular editions of translations to fill in the corresponding gaps in this knowledge.

In the long run it can be expected that the utilization of the huge number of scientists and technicians, as compared with European conditions, supplemented with exceptional quality experts should lead to success. The mighty utilization of scientific-technological personnel gives it a possibility for scope of planning of the many research projects, which would be next to unthinkable in Western Europe.

Research Aims

Among the many problems worked on in the USSR in the field of high polymer research there are several which appear prominently.

Great stress is placed on investigation and technical development of silicones. Silicones are a type of synthetic which were first developed in the US about ten years ago. They are distinguished by their high resistance to high and low temperatures. Their polymer chains do not consist of carbon atoms but of an alternating succession of oxygen and silicon atoms, to which are attached organic groups that can be reactive under certain conditions. Silicones (polysiloxanes) are prepared from silanes having various reactive groups. By varying these groups the properties of silicones can be varied considerably, and they can be suited for special requirements. Basically, it is possible to make very cold resistant lubricants and rubber from silicones usable at a very low and very high temperature and which have a considerable importance for the technical equipment of the modern motorized armies. There are very many reports published in the USSR regarding silane and polysiloxane having various structural groupings. Especially prominent is K. A. Andrianov's school. Andrianov has also developed completely new types of high polymers which contain in the polymer chain not only silicon but also other elements (titanium, aluminum, and others).

Lately a certain class of metalo-organic catalyst has had a continuously increasing importance for the whole synthetics technology. First, with their use the polyolefins can be polymerized at low temperatures (heretofore it had been possible to prepare polyethylene only at pressures of several hundred atmospheres); secondly, they make it possible to prepare structurally very regular polymers. These catalysts were discovered by Ziegler in the Max Plank Institute for Coal Research in Mulheim/Ruhr. After the great technical importance of the socalled Ziegler catalysts (triethyl-aluminum and titanium tetrachloride complexes) had been shown, the USSR also has started an active research program to enlarge this class of catalysts and to find metalo-organic compounds which are less inflammable than triethylaluminum. Shortly thereafter triisobutylaluminum (Kranzel, B. A., Topchiyev, A. N., Siderova, L. G., Izv. Akad. Nauk. Otd. Khimicheskikh Nauk, p 500, April 1958) was shown by Topchiyev and coworkers to be a less dangerous but more active catalyst for propylene polymerization. Topchiyev and Dolgoplosk have especially excelled in catalyst research. The problem of Ziegler catalysts is in a certain relationship with the recently successful preparation of the so-called synthetic natural rubber (1, 4-cis-polyisoprene) which will be considered below.

Great stress has been placed on cellulose research. Cellulose and its derivatives are important raw materials for several important types of synthetics (fibers, films, etc.). An indication of the importance ascribed to cellulose research in the USSR is that Prof Danilov, chief of the laboratory for cellulose chemistry at the Academy Institute for High Polymer Compounds, Leningrad, is also the director of the whole institute.

The 20th Congress CPSU also formulated directions for the chemical industry within the framework of the Sixth Five-Year Plan; they emphasized the importance of providing raw materials for synthetics industry. Processes for improving and increasing the production of ethylene, propylene, butylene, butadiene, isoprene, etc., is to be developed vigorously, as also new methods for cracking [of hydrocarbons]. In order to rationalize their management, plants of petroleum and chemical industries are to be combined into the so-called combinates. Special importance is given to increased production of acetylene. With respect to the already mentioned importance of glass fibers for the synthetics industry, the production of alkali-free glass is to be multiplied. Polyester and ethoxyline resins reinforced with glass fibers, and also silicone are of a great importance lately for the construction of remote control rockets. It should be assumed that the stimulus for extensive research and development programs comes from this area, as is the case in the US.

Contrary to all expectations, the low pressure polyethylene, prepared by using Ziegler catalysts, is not cheaper than the one prepared by the old high pressure method. The perfection of the low pressure method should be accelerated in order to expect a reduction in price. Considerable attention will also be given to the development of fluoro-organic polymers which have shown unusual resistance to chemicals and have a number of possibilities for special utilization in modern war technology.

The Soviet synthetics technology appears to be on a level which is barely below that of the western world. All standard types of synthetics produced in Western Europe and in the US, such as polyethylene, polystyrene, polyvinylchloride, polyamide (nylon), glass fiber reinforced polyesters, and polyfluorocarbons are manufactured in the USSR. Soviet scientists are also in a position to produce in a laboratory or on a pilot plant scale the types which probably are not yet manufactured on an industrial scale. Since last year the isotactic polypropylene has been supplied by Montecatini (Italy) and by Farbwerken Hoechst [Western Germany]; however, Topchiyev (Topchiyev, A. V., Kranzel, B. A., Tolchinskiy, I. M., and Garnishevskaya, G. G., Dokl. Akad. Nauk SSSR, Vol 114, P 113 (1957)) also experimented with this regularly structured polymer and published the necessary conditions for polymerization as developed in his laboratory.

The high technological level in the area of reinforced polyester and epoxy resins promote the already highly developed Soviet rocket technology. With respect to the aviation technology and high frequency technology associated with it, it should be assumed that in the USSR also dielectrics have been produced which are resistant to high temper-

atures, oils and chemicals; the same applies also to rubber types which are not affected by oils and fuels.

Probably the production of the synthetics which are used primarily for the consumer goods industry and for household articles (like polyethylene or polystyrene) is not as large as that in the Western world, but according to official reports, these production figures will be multiplied in the future. The Russian natural gas resources and the developed petroleum chemistry provide sufficient amounts of raw materials.

In Soviet professional publications, not much can be found about the actual state of development of the synthetics industry, and almost no production figures. However, much can be read about the development goals and expectations for the future. M. Garber (Garbar, M. Y., Khimicheskaya Promishlennost', p 397, Oct/Nov 1957) gives some relative values regarding the development of synthetics and chemical industries in the USSR: Soviet Industry Production Indices for the Years 1940 to 1956 (index for 1940 = 100).

	1950	1955	1956
Industry total	173	320	350
Chemical industry	183	416	350
Synthetics industry	300	738	855

Regardless of the considerable success of the Soviet synthetics industry development, there appears to be shortages in the productivity and plant equipment. A group of British engineers who visited plants of the Soviet synthetics industry last year observed, among other things, the absence of safety installations for machinery and deficient accident prevention; such safety installations are regularly used in Europe.

Rubber

Artificial rubber, strictly speaking, is nothing else than a special category of synthetics. But because of certain properties, it is considered by many as an independent class of material next to both main groups of synthetics -- the thermoplastics and the thermosetting resins.

In the USSR the production of synthetic rubber has been much promoted for a long time and the respective technology early achieved a high standard. The first important step was S. B. Lebedev's developed synthetic method for rubber preparation from butadiene (butadiene can be obtained from ethyl alcohol by a catalytic process). Already in 1931, the USSR started construction of the first synthetic rubber production plant. In July 1932 the first 400 kilograms of Soviet synthetic rubber were produced in the Yaroslav plant. The rubber plant in Voronezh started producing in May 1933. The variety of the presently produced rubber types in the USSR is really extensive and suited to a number of

special requirements. Some rubber types are produced in the USSR only. The largest part of the manufactured rubber is based on butadiene, and, indeed, similarly to the western world method, it is a copolymer with styrene and acrylonitrile.

Before World War II there were produced in the USSR only three types of synthetic rubber: a sodium butadiene rubber (SKB), a chloroprene rubber, and a butadiene rubber in latex form. After the war there followed a large increase in the total production and in the number of types. Since 1950, next to the above mentioned types of rubber, there are produced a butadiene-vinylidene chloride copolymer (DVKhB-70), a butadiene-acrylonitrile rubber (SKN) in three types, a chloroprene latex (SKBM), and, the most important -- the butadiene-styrene copolymer (SKS-30). In the past few years there has been added a whole line of other rubber types, the detailed enumeration of which would be excessive here. However, the butadiene-1-methylstyrene copolymer (SKMS-30) should be mentioned; presently it is produced only in the USSR and it shows a number of advantages in comparison with SKS-30. The SKS-30 corresponds to the GR-S types known in the US. Silicone rubber (SKT) production was started in 1956. This rubber can be used in the temperature range from minus 60 degrees to plus 250 degrees centigrade, like the US silicone rubber types. In 1956, production was also started of butyl and brom-butyl rubbers.

Special attention should be given to the emphasis on the accelerated development of the so-called SKI rubber. It is known that the prepared synthetic rubber types based on the polymerization of butadiene cannot replace natural rubber in any respect. Natural rubber has a combination of mechanical properties which has been impossible to achieve with any synthetic rubber type up to now. Butadiene rubber, especially, is not equal to natural rubber with respect to wear and elasticity. But now the 1,4-cis-polyisoprene of the natural rubber (chemically speaking) can form an almost ideal regularity in its structure. It was not possible to prepare structurally completely regular rubber types until the discovery of the Ziegler catalysts and their further development in the direction of stereospecific activity by Natta. By the end of 1955, the US had succeeded in preparing structurally regular 1,4-cis-polyisoprene, i.e., if one may be permitted to say, to prepare "synthetic natural rubber", with the Ziegler catalysts and also by using lithium dispersions. These syntheses indicate significant research and technological power and were rightly acknowledged as a great achievement. It also appears that the synthetic 1,4-cis-polyisoprene not only has a microstructure similar to natural rubber, but also it is similar to it regarding macroscopic physical properties.

However, similar research has been conducted also in the USSR and it has brought the same success as in the US. The Research Institute for Synthetic Rubber, with the research teams of Korotkov and Dolgoplosk, have made the main contributions here. Russian authors indicate that the technical development of 1,4-cis-polyisoprenes is farther advanced in the USSR than in the US. Actually the natural rubber in the US is rather cheap. It is much harder to obtain the isoprene monomer than butadiene.

Therefore it should be assumed that 1,4-cis-polyisoprene will not become an important competitor for natural or butadiene rubbers.

Because of this, American research has not advanced farther than the pilot plant stage. In the USSR, however, it is emphasized that they have succeeded in developing a technological method for large-scale production, following Korotkov's suggestions. In the Sixth Five-Year Plan, industrial production of 1,4-cis-polyisoprene has been declared as one of the main goals. The essential problem here is the production of cheap isoprene monomer. Three methods have been discussed in Soviet scientific literature:

1. Dehydrogenation of isopentane,

2. The method by Favorskiy, based on the preparation of dimethylacetylenylcarbine [3-methylbutyne-1-01-3], its hydrogenation to dimetylvinylcarbinol, and further dehydration to isoprene,

3. A method discussed also by American scientists -- preparation of isoprene by a condensation of formaldehyde and isobutyl alcohol; commercially this method is being considered the least important, though.

Since in the USSR, economic decisions made are based less on cost than on other considerations, it should be assumed that the industrial production of the "synthetic natural rubber" will be successful, especially because the huge natural gas resources and the waste products of the petroleum industry supply sufficient raw material for the preparation of isoprene. In this manner the Soviet Union would secure for itself a material which is equal to natural rubber and would become independent of imports from southern countries.

- END -

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